

310
In5

INGRAM

An accurate determination of the
freezing point curve of aqueous
solutions of chloral hydrate

Chemical Engineering

B. S.

1910

UNIV. OF
ILLINOIS
LIBRARY

UNIVERSITY OF ILLINOIS
LIBRARY

Class

Book

Volume

1910

In 5

Mr10-20M



870
1214/4

AN ACCURATE DETERMINATION OF THE FREEZING
POINT CURVE OF AQUEOUS SOLUTIONS
OF CHLORAL HYDRATE

BY

HAROLD STUART INGRAM

THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMICAL ENGINEERING

IN THE

COLLEGE OF SCIENCE

OF THE

UNIVERSITY OF ILLINOIS

Presented June, 1910 ~

1710
1915

wa F 11 (Trang)

UNIVERSITY OF ILLINOIS

June 1,

1900

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Harold Stuart Ingran

ENTITLED An Accurate Determination of the Freezing Point Curve of Aqueous

Solutions of Chloral Hydrate

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Chemical Engineering

E. H. Washburn

Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry


168112

Purpose of the Investigation.

The work here recorded was undertaken with the object of obtaining data for an accurate freezing point curve of aqueous solutions of chloral hydrate. Work along this line had been done by Loomis (Z. physikal. Chem. 32 p. 600, 1900) on dilute solutions and on more concentrated ones by Abegg (Z. physikal. Chem. 15 p. 208, 1894). The work of Loomis was accurate but as there is some question as to the accuracy of that of Abegg the present investigation was undertaken for the purpose of checking his results. Reference was had to various articles on the subject of freezing point determinations, those which were especially consulted being the following: "Das System, Chloral und Wasser" by C. von Rossem (Z. physikal. Chem. 62 p. 681, 1908); "Hydrates in Solution" by H.C. Jones; "Studien über Gefrierpunkte konzentrierter Lösungen" R. Abegg (Z. physikal. Chem. 15 p. 208, 1894); and "Gefrierpunkterniedrigungen durch Nichtelectrolyte in konzentrierten wässrigen Lösungen" by W.A. Roth (Z. physikal. Chem. 42 p. 560, 1903).

Preparation of the Chloral Hydrate.

The chloral hydrate was prepared from Kahlbaums chloral by adding it to the theoretical amount of water required to form the hydrate. The hydrate was then crystallized several times from chloroform and the crystals so obtained were dried in a desiccator over a mixture of chloral and chloral hydrate.



Digitized by the Internet Archive
in 2013

<http://archive.org/details/accuratedetermin00ingr>

Methods of Analysis

The first part of the work consisted in testing several titrametric methods for determining the chloral hydrate content of the solutions. In the one first tried the hydrate was decomposed by means of NaOH and the excess of alkali titrated back with a standard acid. This method is an unsatisfactory one, both as regards the length of time for the reaction and the accuracy of the determination. The time required is at least five hours and the error may vary from 1 to 5 percent depending on the amount of substance taken.

In the next method considered the hydrate was oxidized by a solution of KMnO_4 . By this reaction there is formed trichloroacetic acid, the end point being determined by the change in the color of the solution. This is the reaction given by Clermont (Chem. Central-blatt 42 2 p.534,1871) and Berichte 9 p. 191) This seemed to be a promising method and it was accordingly taken up with a view of using it in the analysis of the solutions.

The KMnO_4 was prepared according to the directions on page 133 in Suttons Volumetric Analysis. In the first attempt to test this method the reaction was carried out at room temperature. There was some reaction as indicated by the color changes but in no case was there complete oxidation to the acid as indicated by the amount of KMnO_4 used. Since the reaction appeared to be incomplete at room temperatures, the solutions were next heated to boiling before adding the KMnO_4 . Under these conditions the reaction was found to be complete but there was also evidence that decomposition was taking place and that the end products were

chlorine or hydrochloric acid rather than trichloroacetic acid. A number of trials were made but all gave unsatisfactory results and the method was abandoned. There was every evidence that the trichloroacetic acid was formed but that the reaction did not stop sharply at this point.

Preparation of a Density Curve.

The method finally used was one where-in solutions of known strength were made up and their densities determined. From the data so obtained a density-molecular-concentration curve was drawn from which the chloral hydrate content of a solution may be obtained by determining its density and interpolating on the curve. Eight solutions were prepared, varying in concentration from 0.0299 molal to 3 molal, by weighing out the crystals and adding them to the required amount of pure distilled water. The pycnometer used was the Ostwald form of the Sprengel type and glass caps were placed over the capillaries to prevent evaporation. The pycnometer was first cleaned and dried and its weight empty determined against a counterpoise. This was called weight W_1 . The instrument was then filled with pure distilled water and immersed in a thermostat at a temperature of 25° . When the water had become heated to the temperature of the bath the meniscus in the capillary was drawn along to the mark and the pycnometer taken out, dried and weighed. This weight was called W_2 . This operation was then repeated using the solution whose density was to be determined. This gave a third weight W_3 . From these weights the density of the solution determined by the formula,

$$D_{25}^{25} = \frac{(W_3 - W_1)(0.99707)}{W_2 - W_1}$$

The thermostat mentioned consisted of a large battery jar in which was placed an electric lamp to keep the bath at the required temperature, 25°C . The water in the thermostat was kept in constant agitation by a propeller run by an electric motor. The temperature was read off by means of a Beckmann thermometer, which had been compared with a standard thermometer calibrated at the National Bureau of Standards, and was regulated to $1/100$ of a degree. The density was in all cases referred to that of water at 4° . The results are given in Table 1.

Freezing Point Measurements.

The density curve having been obtained the next step was the determination of the freezing point lowerings. The apparatus used consisted of a Dewar tube enclosed in a glass cylinder. This glass cylinder was filled with a mixture of ice and water thus making the temperature of the surroundings very constant. The top of the tube was closed by a cork thru which was inserted a Beckmann thermometer, a glass tube for drawing off samples of the solutions for density determinations and a glass stirrer. The thermometer was continually tapped by an electric tapper during the readings and the solution was stirred thoroly.

The "modus operandi" was as follows: the Dewar tube was placed in the glass cylinder and the latter filled with cracked ice and water. The solution of the hydrate, previously cooled down to its freezing point, was then poured into the Dewar tube-- which had been previously half filled with pure fine ice-- and the cork carrying the thermometer, stirrer and sampling tube inserted. The tapper was started going and the solution stirred constantly

until the reading of the thermometer showed no change. The temperature was then recorded and a sample of about 100 c.c. drawn off. An amount of water equal to that drawn off was then added and a new reading taken. This was repeated till a sufficient number of readings was obtained. The first solution was that of the greatest concentration and the temperature readings became higher as the dilution increased.

The densities of the samples drawn off were determined by the method before described. From the density determinations the molecular concentration of the solution was found by interpolation on the curve.

As the highest concentration in the first set of data was only 1.751 molal a second series of readings was taken. The greatest concentration in this case was 2.9624 molal giving a lowering of 5.957°C . The values of the freezing point lowerings and molecular concentrations obtained in these two series of readings together with the data obtained by Loomis(*loc. cit.*) are recorded in Table 2, the curve obtained being shown in figure 2. From this curve Table 3 was prepared showing the variation in lowering by .1 mol variation in the concentration.

Conclusion

From consideration of the data and the appended curves it is seen that as the concentration of the solution increases the freezing point lowering also increases but not proportionally. This latter point is shown by taking the ratio of Δt to n' , which, if the lowering were proportional to the concentration should be constant. This constant in the case of water is 1.86° . Tho the

substance under consideration shows a rather marked deviation from this constant based on the equation of Raoult, such a result is to be expected when it is remembered that the equation is supposed to hold only for very dilute solutions.

The theoretical equation connecting a freezing point lowering (Δt) with the mol fraction N' of solute for the simplest type of ^{an aqueous} solution is,

$$N' = 0.0096895(\Delta t - 0.00425\Delta t^2)$$

where N' is the ratio of the number of mols of the substance in question to the total number of mols present in the mixture, and Δt is the observed lowering of the freezing point. This equation was derived by Edward W. Washburn (Technology Quarterly XXI, No. 4 Dec. 1908). The graph of this equation is shown in figure 3. together with data for aqueous solutions of chloral hydrate. When however we make use of the theoretical equation we see that the results show good agreement even for the most concentrated solutions. This would seem to indicate that in the case of chloral hydrate there was neither ionization nor hydration of the substance.

Table No. 1

Data for Density Curve.

Molecular Concentration	Density
2.9915	1.2123
2.0013	1.1426
1.0003	1.0676
.5037	1.0316
.2474	1.0141
.1257	1.0037
.0626	1.0021
.0299	1.0012

Table No. 2.

Data for Freezing Point Curve.

Density	Molecular Concentration	Lowering	Molecular Lowering
1.2103	2.9624 ✓	5.957	2.011
1.1948	2.7417 ✓	5.487	2.000
1.1743	2.4521 ✓	4.832	1.971
1.1231	1.7896 ✓	3.448	1.921
1.1213	1.7512 ✓	3.309	1.890
1.1130	1.6447 ✓	3.125	1.900
1.1026	1.4983 ✓	2.817	1.880
1.0909	1.3326 ✓	2.512	1.885
1.0780	1.2061 ✓	2.201	1.873
1.0681	1.0581 ✓	1.983	1.874
1.0600	.8545 ✓	1.621	1.837
1.0436	.6215 ✓	1.100	1.867

The following values are from Loomis.

.2000	.3760	1.88
.1000	.1875	1.87
.0500	.0924	1.85
.0200	.0373	1.87
.0100	.0186	1.86

Table No. 3.

Showing Variations with .1 mol Variation in Concentration.

Molecular Concentration	Density	Lowering	Molecular Lowering	Mol Percent 100 N'
.1000	1.0072	.1875	1.875	.0830
.2000	1.0143	.3760	1.880	.3590
.3000	1.0213	.5650	1.890	.5000
.4000	1.0281	.7500	1.870	.7200
.5000	1.0349	.9400	1.880	.8970
.6000	1.0421	1.1300	1.883	1.0750
.7000	1.04920	1.3200	1.885	1.2260
.8000	1.0563	1.5480	1.935	1.4790
.9000	1.0634	1.6920	1.880	1.6300
1.0000	1.0705	1.8810	1.881	1.7290
1.1000		2.0700	1.881	1.9720
1.2000		2.2530	1.877	2.1520
1.3000		2.4400	1.876	2.3400
1.4000		2.6280	1.877	2.5180
1.5000	1.1060	2.8200	1.880	2.7100
1.6000		3.0100	1.881	2.8940
1.7000		3.2040	1.884	3.0860
1.8000		3.3980	1.887	3.2710
1.9000		3.5990	1.894	3.4600
2.0000	1.1416	3.8020	1.901	3.6600
2.1000		4.0100	1.909	3.8600
2.2000		4.2250	1.920	4.0690
2.3000		4.4410	1.930	4.2810
2.4000		4.6600	1.941	4.4910
2.5000	1.1796	4.8860	1.954	4.7000

Table No.3(continued)

Molecular Concentration	Density	Lowering	Molecular Lowering	MolPercent 100 N'
2.6000		5.115	1.265	5.0150
2.7000		5.350	1.285	5.1500
2.8000		5.583	1.282	5.3660
2.9000		5.820	2.006	5.5920

Figure 1.
Density Curve.

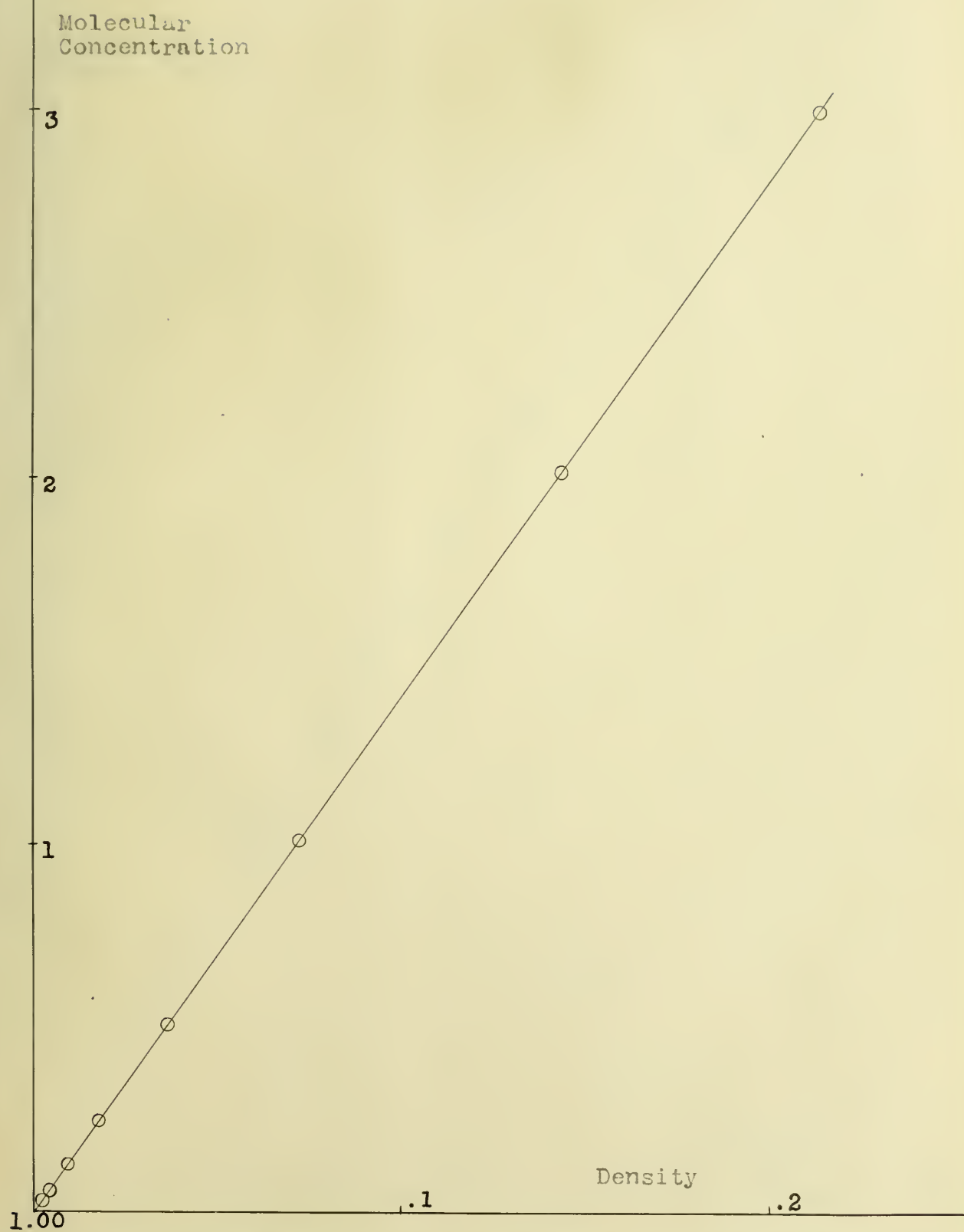


Figure 2.

Molecular Concentration-Lowering
Curve

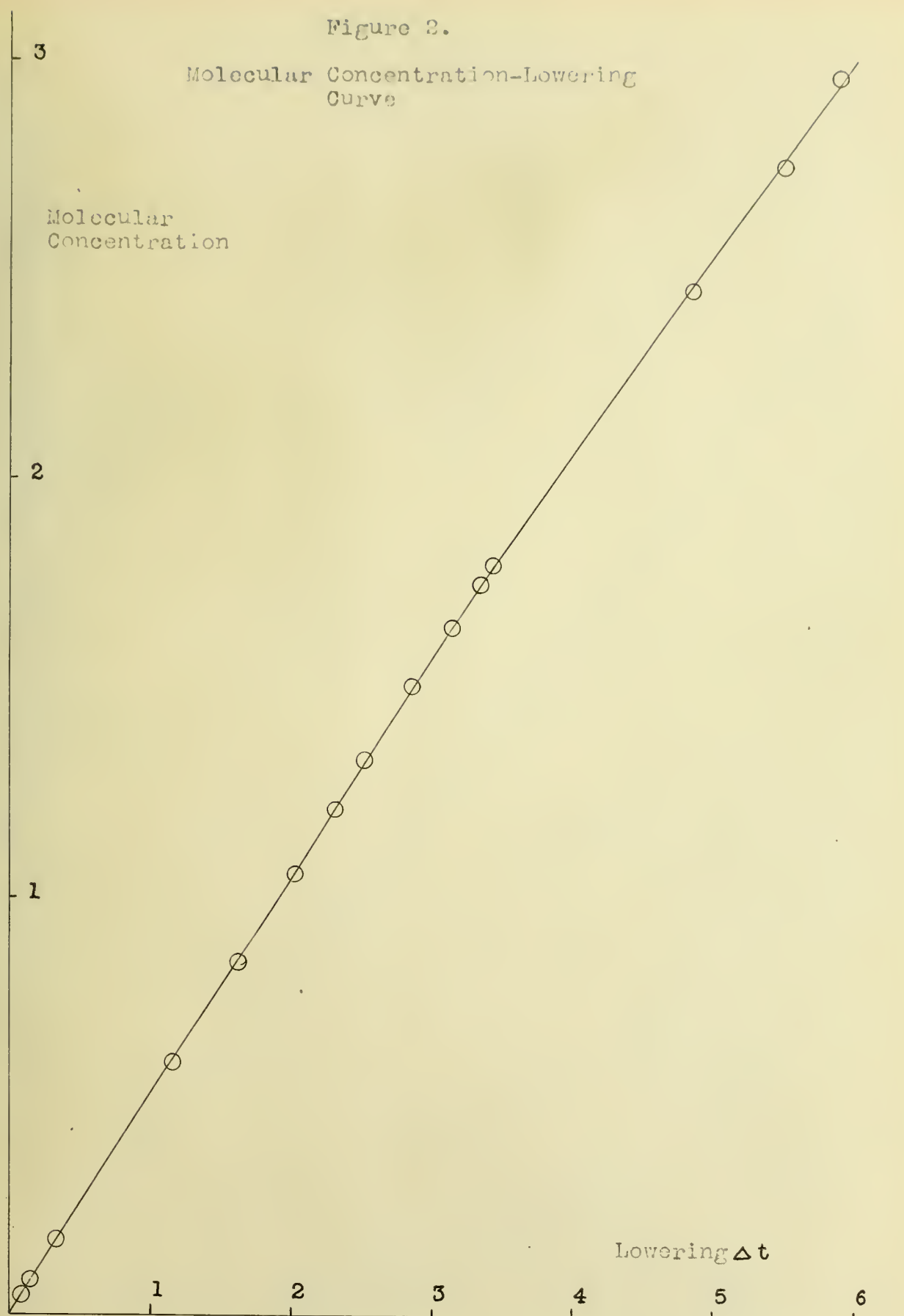
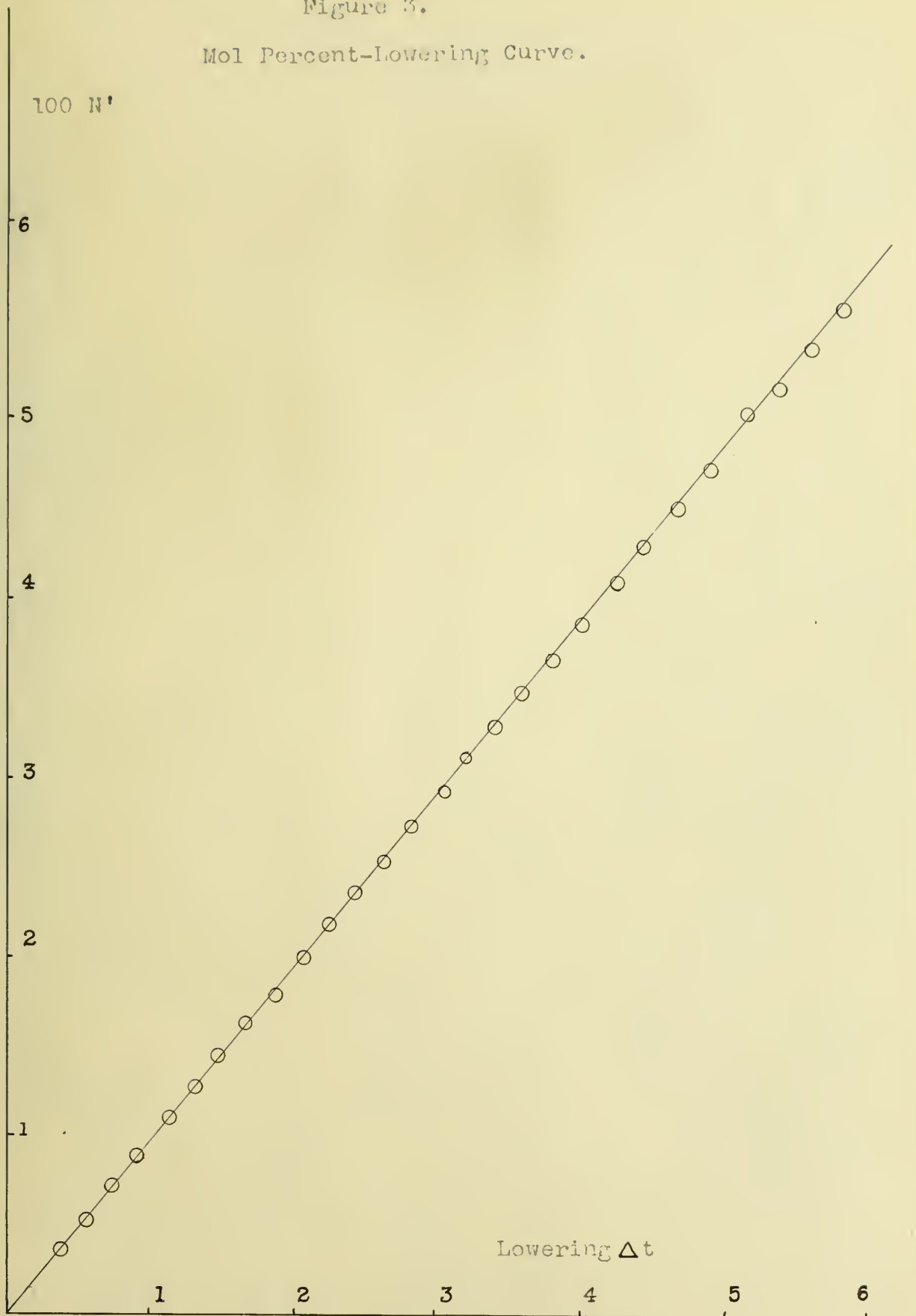


Figure 3.

Mol Percent-Lowering Curve.







UNIVERSITY OF ILLINOIS-URBANA



3 0112 079094147